Influence of carbon substitution on the heat transport in single crystalline MgB_2

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We report data on the thermal conductivity $\kappa(T,H)$ in the basal plane of hexagonal single-crystalline and superconducting $Mg(B_{1-x}C_x)_2$ ($x = 0.03, 0.06$) at temperatures between 0.5 and 50 K, and in external magnetic fields H between 0 and 50 kOe. The substitution of carbon for boron leads to a considerable reduction of the electronic heat transport, while the phonon thermal conductivity seems to be much less sensitive to impurities. The introduction of carbon enhances mostly the intraband scattering in the σ-band. In contrast to the previously observed anomalous behavior of pure MgB_2, the Wiedemann-Franz law is valid for $Mg(B_{0.94}C_{0.06})_2$ at low temperatures.

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The superconducting state of MgB_2 is characterized by at least two gaps in the electronic excitation spectrum, both of significantly different width (for a review, see Ref. 1 and references therein). The larger energy gap, Δ_σ, develops on quasi-two dimensional (2D) sheets of the Fermi surface, often denoted as σ-band. A distinctly smaller gap Δ_π is formed on 3D parts of the Fermi surface that are related with the so-called π-band. Amazingly, lattice disorder, which is thought to lead to interband scattering and consequently to an equalization of gap amplitudes[2] has very little effect on the two-gap nature of superconductivity in MgB_2. For example, the residual resistivity ρ_0, which provides a measure of impurity scattering, varies by orders of magnitude in different MgB_2 samples but no significant concomitant variation of T_c is observed. The difference in the symmetry of the orbitals forming the quoted bands in MgB_2 was suggested to be the reason for weak *interband* scattering.[3] The *intraband* scattering rates in each band may lead to different mean free paths in each band but will not affect the multigap nature of the superconducting state. Current studies of MgB_2 aim at a controlled variation of the influence of interband and intraband scattering processes on physical properties of MgB_2. One way of achieving this is provided by selected small variations of the chemical composition, leading to selective variations in the quoted scattering processes. In particular, carbon substitution for boron is expected to enhance the intraband scattering rate mostly in the σ-band, which is formed by the boron sp_xp_y orbitals, but it does not alter the interband scattering very much because carbon impurities do not generate considerable out-of-plane distortions.[4] Various experimental results support the persistence of two different gaps in $Mg(B_{1-x}C_x)_2$ up to $x \approx 0.1$,[5,6,7,8,9] but conflicting results are reported for higher carbon concentrations.[8,9] Carbon doping is also reported to cause a considerable increase of the upper critical field and some reduction of its anisotropy.[10,11,12,13]

In previous work it was demonstrated that important aspects of multigap superconductivity in MgB_2 can experimentally be addressed by measurements of the thermal conductivity κ as a function of temperature T and external magnetic field H.[14,15,16,17,18,19,20] Particularly useful are $\kappa(H)$ data in the mixed state,[19] because they allow for distinguishing between the contributions of the different bands to the electronic heat transport and the scattering of phonons by electrons. Accompanying theoretical considerations[21,22,23,24] support these interpretations.

In this paper, we present a set of $\kappa(T,H)$ data obtained for single crystals of $Mg(B_{1-x}C_x)_2$ ($x = 0.03, 0.06$) in the basal plane of the hexagonal crystal structure and we compare them with our previously published, analogous data for pure MgB_2. The crystals were grown with a high-pressure technique in a cubic anvil press as described in Ref. 13. Two approximately bar-shaped single crystals with dimensions of $0.8 \times 0.27 \times 0.10$ mm^3 for $Mg(B_{0.97}C_{0.03})_2$ and $0.9 \times 0.26 \times 0.13$ mm^3 for $Mg(B_{0.94}C_{0.06})_2$ were selected for the thermal conductivity measurements. For both samples, the shortest extension in size is along the c-axis. The high structural quality and the homogeneity of the carbon distribution were confirmed by single-crystal X-ray diffraction and EDX analyses on similar crystals from the same batches. A standard uniaxial heat-flow method was used for measuring $\kappa(T,H)$, with the same experimental arrangements as reported in our previous works on pure MgB_2.[18,19] The $Mg(B_{0.94}C_{0.06})_2$ sample was also used for 4-contact *dc* measurements of the electrical resistivity.

The temperature dependences of thermal conductivities of carbon-doped MgB_2 in zero magnetic field and $H = 50$ kOe are presented in Fig. 1. For comparison, our earlier data[19] for pure MgB_2 are also shown. The substitution of carbon for boron results in a considerable reduction of the zero-field thermal conductivity, mainly in the vicinity and above T_c. For the C-doped samples we note a distinct change in $\partial\kappa/\partial T$ at T_c, in contrast to the previously noted, striking absence of any such feature at T_c of undoped MgB_2.[14,15,16,17,19]

Selected $\kappa(H)$ data at several fixed temperatures for x=0, 0.03, and 0.06 are shown in Fig. 2. At 0.6 K, $\kappa(H)$ is reversible above at least 1 kOe and at higher temperatures, the irreversibility field decreases. In what follows, we only discuss the $\kappa(H)$ curves in the reversible region above H_{c1}. Increasing H above H_{c1} leads, at all tem-

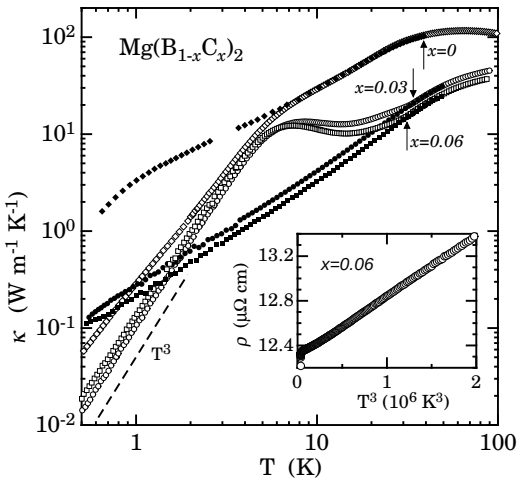

FIG. 1: Thermal conductivity *vs* temperature in the *ab*-plane of single-crystalline $Mg(B_{1-x}C_x)_2$ ($x = 0, 0.03, 0.06$) in zero magnetic field (open symbols) and $H \parallel c = 50$ kOe (solid symbols). The arrows indicate the zero-field critical temperature T_c. The inset emphasizes the T^3 variation of the in-plane electrical resistivity $\rho(T)$ of $Mg(B_{0.94}C_{0.06})_2$.

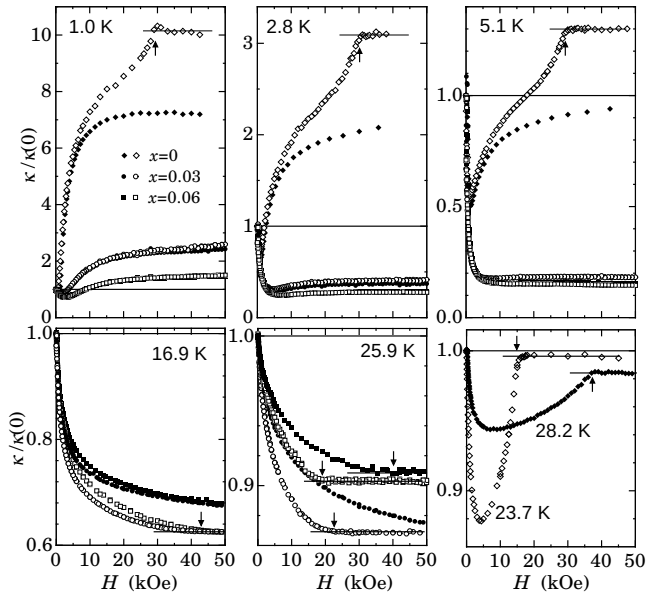

FIG. 2: Thermal conductivity in the basal plane of $Mg(B_{1-x}C_x)_2$ (x=0, 0.03 and 0.06) vs H at several fixed temperatures. The arrows indicate the upper critical field H_{c2}. The closed and open symbols correspond to the field directions perpendicular and parallel to the $c-$axis, respectively.

peratures, to an initial decrease of κ. With further increasing H, κ increases and, when H exceeds the upper critical field H_{c2}, the thermal conductivity is practically independent of field. At $T \ll T_c$, $\kappa(H)$ for pure MgB_2 depends very little on the orientation of the magnetic field below about 5-10 kOe, but in higher fields, the κ values for $H \parallel c$ exceed those for $H \perp c$ significantly (see the upper row in Fig. 2). For the carbon-doped samples, $\kappa(H)$ depends only weakly on the field orientation in all fields. Another striking observation across the entire covered temperature range is the much weaker field-induced enhancement of κ for the carbon-doped samples than for pure MgB_2. At temperatures above about 5 K and for $x = 0.03$ and $x = 0.06$, no field-induced enhancement of κ is observed at all, whereas for $x = 0$, it persists at all temperatures up to T_c (see the lower row in Fig. 2).

The $\kappa(H)$ curves allow to establish the values of the bulk upper critical field H_{c2} via the onset of the field independence of $\kappa(H)$ (see arrows in Fig. 2). The resulting $H_{c2}(T)$ data are shown in Fig. 3. They are in agreement with results of torque measurements on similar samples.[12]

The zero-field electrical resistivity for the $x = 0.06$ sample was measured between 4.2 and 130 K. The transition at T_c=32.9 K is, with a width of about 0.1 K, rather narrow. In the entire covered temperature range above T_c, $\rho(T)$ is well described by $\rho = \rho_0 + aT^3$ (see the inset in Fig. 1) where two scattering processes, associated with quasiparticle scattering by defects and phonons, respectively, are considered. The constant parameters are $\rho_0 = 12.3\ \mu\Omega$cm and $a = 5.4 \times 10^{-7}\ \mu\Omega$cmK^{-3}. In comparison, for pure MgB_2, $\rho_0 = 2.0\ \mu\Omega$cm and $a = 6.7 \times 10^{-7}\ \mu\Omega$cmK^{-3} (Ref. 19), which demonstrates that carbon doping strongly enhances the scattering by defects, while the electron-phonon scattering is only weakly altered.

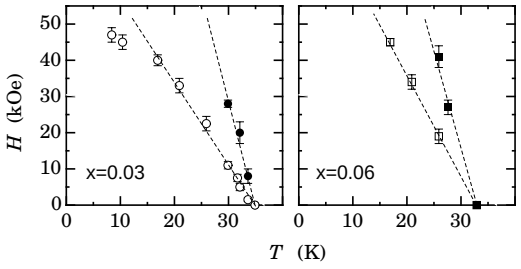

FIG. 3: The upper critical fields $H_{c2}(T)$ as evaluated from thermal conductivity data (open symbols for $H \parallel c$ and solid symbols for $H \perp c$). The dashed lines are to guide the eye.

Because we assume that the transport is provided by itinerant electronic (κ_e) and lattice excitations ($\kappa_{\rm ph}$), such that $\kappa = \kappa_e + \kappa_{\rm ph}$, any analysis of the changes of $\kappa(T, H)$ caused by the substitution of carbon for boron should consider corresponding changes in both these channels. In MgB_2, the electronic thermal conduction consists of contributions from both the σ- and the π-band, hence $\kappa_e = \kappa_{e,\sigma} + \kappa_{e,\pi}$.[21,22,23,24] When the temperature is reduced to below T_c in zero magnetic field, the continuous reduction of the number of unpaired quasiparticles leads to a decrease of κ_e but, because of

the reduction of the scattering of phonons by electrons (holes), also to an increase of $\kappa_{\rm ph}$. Altogether, the features of $\kappa(T)$ depend on the relative magnitudes of κ_e and $\kappa_{\rm ph}$ and on the efficiency of phonon scattering by electrons. Since for MgB_2 the energy gap in the π-band at a given normalized temperature T/T_c is considerably smaller than expected from the BCS-theory, the π-band contributions to both the heat transport and the phonon scattering extend to lower temperatures than in conventional superconductors. Nevertheless, both $\kappa_{e,\sigma}$ and $\kappa_{e,\pi}$ are negligible at very low temperatures and $H = 0$. Below 2-3 K, the observed $\kappa(T, 0)$ varies approximately as T^3 (see dashed line in Fig. 1), which is expected for purely phononic conductivity and a dominant scattering of phonons at the sample boundaries. The observation that the $\kappa(T, 0)$ curves tend to merge below T_c suggests that carbon doping does not influence the thermal conduction via phonons very much, and that the difference in $\kappa(T, 0)$ observed at higher temperatures results from κ_e being considerably reduced by the introduction of carbon for boron. The question of which band is more strongly influenced by doping, can be answered by analyzing the $\kappa(H)$ data in the mixed state.

The quasiparticles associated with the vortices provide additional scattering of phonons and also enhance κ_e. The competition of these two mechanisms results in typical $\kappa(H)$ curves for type-II superconductors, with an initial drop of κ when H is raised to above H_{c1} and subsequently to a considerable increase when H approaches H_{c2}. For MgB_2 this rather gradual increase of $\kappa_e(H)$ is replaced by an extremely rapid increase of κ_e at fields $H \ll H_{c2}$, followed by a saturation region and yet another increase in the vicinity of H_{c2}.[19] The low-field increase does not scale with H/H_{c2} as is observed for conventional superconductors and is almost independent of field orientation, despite the strong anisotropy of H_{c2}. This unique behavior is explained in terms of a two-band scenario, where the smaller energy gap Δ_π is closed at a relatively low and weakly-anisotropic field $H^*_\pi < H_{c2}$, of the order of 10 kOe for pure MgB_2.[25,26,27] Therefore, $\kappa_{e,\pi}$ increases rapidly when the field approaches H^*_π and, still in the mixed state, adopts its normal-state value above H^*_π. The σ-band contribution $\kappa_{e,\sigma}$ only grows when H approaches H_{c2}, the enhancement being strongly anisotropic, reflecting the anisotropy of H_{c2}.

The striking difference between carbon-free and carbon-doped samples is that, for the latter, no significant increase in $\kappa(H)$ is observed in the vicinity of H_{c2}. It implies that $\kappa_{e,\sigma}$ is strongly reduced by carbon substitution from about 50% of the total normal-state κ_e for $x = 0$ (Ref. 19) to a level close to our experimental resolution for $x = 0.03$. Hence, the quasiparticle contribution to the heat transport is dominated by the π-band, i.e., $\kappa_e \approx \kappa_{e,\pi}$. Carbon doping also reduces $\kappa_{e,\pi}$ but less severely than $\kappa_{e,\sigma}$. At 1.0 K and in a field $H \perp c$=45 kOe, the thermal conductivity for the $x = 0.06$ sample is a factor of 11 smaller than for pure MgB_2. Since at such low temperatures and high fields $\kappa_{\rm ph}$ is rather small, this reduction is obviously due to the carbon-doping induced reduction of $\kappa_{e,\pi}$. The quasiparticle thermal conductivity is given by $\kappa_e = C_e v_F \ell/3$, where C_e is the electronic specific heat, v_F the Fermi velocity and ℓ the mean free path. If we assume that by carbon doping at the 6% level neither the electronic density of states at the Fermi level $N_\pi(E_F) \propto C_{e,\pi}$ nor the Fermi velocity $v_{F,\pi}$ in the π-band are much altered, then the reduction of $\kappa_{e,\pi}(x)$ simply reflects the reduction of the corresponding mean free path ℓ_π, due to enhanced scattering by carbon. The reduction of $\kappa_{e,\sigma}$ is at least an order of magnitude stronger, implying a corresponding reduction of the mean free path ℓ_σ. With the same assumptions, the reduction of the mean free path may also be evaluated from the values of the residual electrical resistivity ρ_0. Since both bands contribute to electrical conductivity, the factor $\rho_0(x = 0)/\rho_0(x = 0.06) \approx 6$ represents the reduction of the mean free path, averaged for both bands. The value of this factor is of the same order of magnitude as calculated from $\kappa_{e,\pi}$. This observation corroborates theoretical work of Mazin *et al.*[3] which suggests that the residual resistivity of MgB_2 is mostly due to the intraband scattering of holes in the π-band.

In previous work[19] we reported a significant violation of the Wiedemann-Franz law (WFL) in the field-induced normal state of MgB_2 at low temperatures, below about 6 K. The WFL relates electrical and thermal transport by

$$\kappa_e(T) = L_0 T/\rho(T), \tag{1}$$

where $L_0 = 2.45\times10^{-8}$ W Ω K^{-2}. This relation normally holds for common metals if the relaxation rates for electrical and thermal currents are equal. Elastic scattering of electrons by defects usually guarantees this equality and hence, in the region where this scattering dominates, in particular where $\rho(T) \approx \rho_0$, the validity of the WFL is expected. The Lorenz number $L(T) = \kappa(T)\rho(T)T^{-1}$ where $\kappa(T)$ is the total measured conductivity, is equal to L_0 only if the phonon thermal conductivity is negligible. In the low-temperature normal state of MgB_2, induced by fields $H \parallel c > 30$ kOe, the ratio $L(T)/L_0$ considerably exceeds unity and exhibits a peak at about 1 K, where $L/L_0 \approx 3$.[19] Our estimates for the upper limit of $\kappa_{\rm ph}$ at these temperatures revealed that the phonon contribution to $\kappa(T)$ cannot be responsible for the enhanced Lorenz number, but the cause for the violation of the WFL is not yet firmly established.

For the 6% carbon-doped MgB_2, we cannot exceed the upper critical field at low temperatures with our experimental facilities. A direct evaluation of $L(T)$ in the normal state is thus not possible. However, since in our low-temperature data the quasiparticle contribution $\kappa_e(H)$ saturates to the normal-state values already in the mixed state above H^*_π, $L(T)$ data at fields $H \gg H^*_\pi$ can be used. In Fig. 4, the low-temperature values of $L(T)/L_0$ at $H = 50$ kOe are presented for the $x = 0.06$ sample and, for comparison, for the undoped MgB_2.[19] In both cases, $L(T)$ was calculated as discussed in Ref. 19. In

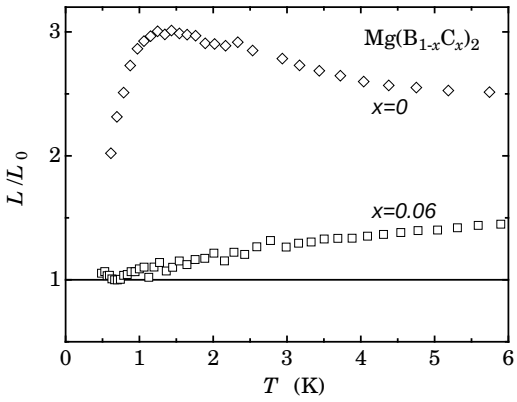

FIG. 4: Normalized Lorenz number $L(T)/L_0$ for $Mg(B_{1-x}C_x)_2$ ($x = 0$ and 0.06).

contrast to pure MgB_2, $L/L_0 \approx 1$ for $Mg(B_{0.94}C_{0.06})_2$ at temperatures $T \lesssim 1$ K. The small deviation at elevated temperatures can naturally be attributed to $\kappa_{\rm ph}$ which, with decreasing temperature, becomes much smaller that κ_e. Thus, at least at low temperatures, no violation of the WFL is observed in the carbon-doped MgB_2. It is important to note that in this case, the heat transport is predominantly carried by the quasiparticles of the quasi-3D π-band. Since in pure MgB_2, where the violation of the WFL is pronounced, both the σ- and the π-band contribute almost equally to the normal-state heat transport, it is natural to conclude that the previously observed anomaly is predominantly tied to the transport in the quasi-2D σ-band. Our results cannot really identify the origin of the violation of the WFL, but they do single out the involved electronic states that are responsible for the effect.

In conclusion, the substitution of carbon for boron leads to a considerable reduction of the electronic thermal conductivity of MgB_2, whereby the transport in the σ-band is much more strongly affected than that in the π-band. The Wiedemann-Franz law, considerably violated for pure MgB_2 at low temperatures, seems to be valid for $Mg(B_{0.94}C_{0.06})_2$.

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